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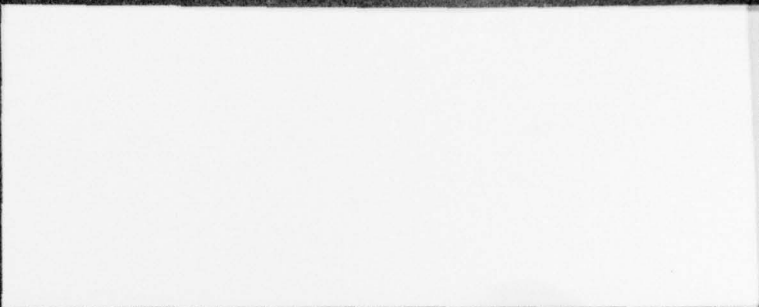
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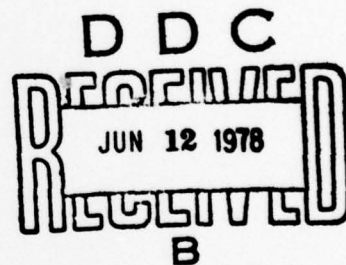
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## Microscopic Flow and Failure Processes in Polymer Glasses

R.J. Morgan and J.E. O'Neal

*Presented at the ACS Division of Organic  
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# Microscopic Flow and Failure Processes in Polymer Glasses\*

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## Introduction

In the aerospace industry, polymeric glasses are utilized in extreme service environments. The need to predict the durability of these materials over long periods without resorting to empiricism requires a detailed understanding of the microscopic flow and failure processes in these glasses and how these processes are modified by the service environment. Flow occurs in polymer glasses either microscopically via crazing or shear banding or macroscopically via necking. This flow absorbs energy during the failure process and enhances the toughness of a polymer glass. The strains in shear bands and crazes are similar [1], and it is uncertain which structural parameters determine if one mode of deformation predominates in a given set of stress-time-temperature conditions.

In this paper we present studies on (i) the microscopic flow and failure processes, (ii) the structural parameters controlling these processes, and (iii) how such processes are modified by the service environment. Our studies cover three different classes of polymer glasses utilized in the aerospace industry, namely:

- (1) Polycarbonate, an amorphous but crystallizable thermoplastic which is utilized as a high-impact-strength transparency.
- (2) Polyimides, the most widely used of the aromatic heterocyclic polymers, process good flame resistance and the ability to withstand high temperatures. These glasses have been utilized in aircraft wire insulation and have acquired limited usage as adhesives and composite matrices.
- (3) Epoxies, crosslinked thermosetting polymers, are the primary materials utilized in adhesives and high-performance polymer-fiber composites.

## Experimental

### Material

The bisphenol A polycarbonate (poly-4,4'-dioxydiphenyl 2,2-propane carbonate) (Lexan, General Electric) used in this study had a viscosity-average molecular weight of 30 000 and contained no significant additives. The polyimides studied were (1) (poly 4,4'-oxydiphenylene) pyromellitimide (Vespel, duPont) (PODPPMI) and (2) a solution-soluble copolyimide based on 3,3',4,4'-benzophenone tetracarboxylic acid anhydride (Upjohn, Polyimide 2080), which is designated here as BTAD-polyimide. Two epoxy systems were studied: (1) diethylene triamine (Eastman)-cured bisphenol-A-diglycidyl ether (Dow, DER 332) epoxy (DGEBE-DETA) and (2) diaminodiphenyl sulfone (Ciba Geigy, Eporal)-cured tetraglycidyl 4,4'-diaminodiphenyl methane (Ciba Geigy, MY720) epoxy (TGDDM-DDS).

### Experiments

The failure processes were monitored by optical and electron microscopy (1) of the fracture topographies and edges of specimens fractured in tension as a function of temperature and strain-rate and (2) of thin films deformed on a metal substrate. In addition, films were strained directly in the electron microscope, and the failure processes were monitored by bright-field microscopy.

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For fracture topography and mechanical property studies, dogbone-shaped specimens were fractured in tension in a table-model tensile tester (Instron TM-S-1130). A scanning reflection electron microscope (JEOL model JEM-100B) and optical microscope (Zeiss UltraphotII) were used for fracture topography studies. Transmission electron microscopy was used for thin-film and carbon-platinum surface replica studies.

## Results and Discussion

### Polycarbonate

Polycarbonate can embrittle, particularly at high strain-rates and for specimens  $< 5$  mm thick, on annealing in the 80-130°C range ( $T_g \approx 150^\circ\text{C}$ ) [2-11]. In tension, this embrittlement is a result of the cessation of shear yielding and macroscopic necking and a reversion to crazing as the predominant deformation and failure mode [5, 10, 12]. This transition is accompanied by a corresponding decrease in molecular flow and energy to failure. The inhibition of molecular flow is a direct result of free-volume decreases produced in bulk specimens on annealing in the glassy state.

Crazing still occurs, however, and plays a predominant role in the failure process when shear yielding is the primary mode of deformation. In Fig. 1, ductile crazes are illustrated along the edges of the necked portion of a polycarbonate glass. We observed from fracture topography studies that failure in the oriented neck often originates from a well-formed craze. Crazes can originate from surface flaws which can be generated by surface crystallization. The ability of polycarbonate to crystallize at and immediately above  $T_g$  allows precrystalline and/or crystalline entities to grow below the bulk  $T_g$  on free surfaces where mobility restrictions are less severe than in the bulk [10]. Surface crystallization causes surface stresses which can produce microcracking. We have directly observed microcracks along the edges of prespherulitic arms. Surface crystallization is enhanced by finger grease and subsequent exposure to  $\sim 100^\circ\text{C}$  [13]. Caird [14] has shown that handling the surface of polycarbonate followed by exposure to  $130^\circ\text{C}$  seriously deteriorates the mechanical properties relative to untouched glasses exposed to the same temperatures.

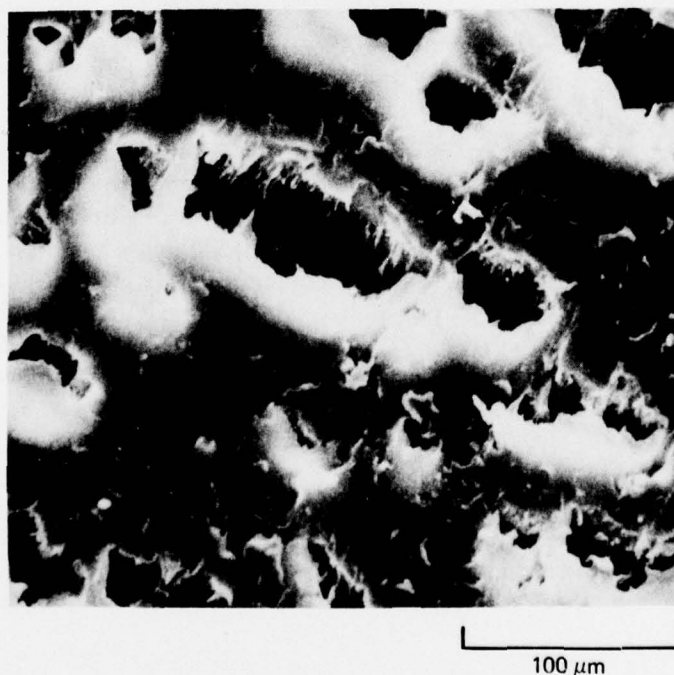


Figure 1 Ductile crazes in the edge of necked portion of polycarbonate.

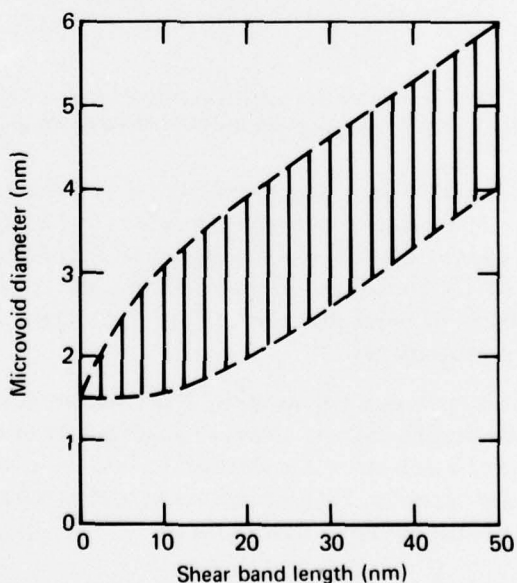
Hence, the flow properties and toughness at a specified strain-rate and thickness of polycarbonate are controlled by (1) the ease of shear-band deformation which depends on free volume and previous thermal history and (2) surface crazes whose characteristics depend on exposure to organics, thermal history, and surface crystallization and fabrication stresses. Therefore, the

desirable toughness of polycarbonate cannot be fully utilized when this glass is exposed to temperatures above 80°C. For many applications, the polycarbonate surface has to be protected by a hard coating to protect this soft glass from the environment. In aerospace transparency service environments, it is often difficult to keep the coating adhered to the polycarbonate.

### Polyimides

In the bulk, both the PODPPMI and BTAD polyimides deform and fail by a crazing process with extensive fibrillation; e.g., all tensile fracture topographies of PODPPMI polyimide fractured from 20-300°C in the  $10^{-2}$  to  $10^{+2}$ /min strain-rate range exhibited features characteristic of a craze-viscous-rupture process.

However, BTAD polyimide films strained directly in the electron microscope exhibited three microscopic modes of deformation: crazing, fine shear-band propagation, and an edge-yielding phenomenon [15]. Edge-yielding, which has some of characteristics of both crazing and shear banding, results in a thinning of the film at the specimen edge. This yielding phenomenon occurred in  $\sim 1 \mu\text{m}$  wide bands which are at an angle of 20-30° to the tensile stress direction. Shear-band deformation occurs in fine bands  $\sim 100 \text{ nm}$  wide. Wu and Li [16] have characterized two shear band deformation processes in polystyrene: one appears as fine shear bands, similar to those we observe in BTAD polyimide, and the other as diffuse shear zones. The fine shear bands in BTAD polyimide exhibit a sharp boundary between themselves and the surrounding undeformed material. From the lack of any contrast differences within the shear bands in bright-field transmission electron microscopy, we conclude that there is uniform shear strain within these bands. Microscopic shear-bands, some of which were  $\sim 1 \text{ nm}$  wide, were found to initiate from 1.5-15 nm diameter microvoids. The length of these shear bands increases with increasing microvoid diameter as shown in Fig. 2. The data scatter in this figure arises from the modification of the shear-band length by the proximity of other microvoids and the  $\sim 100 \text{ nm}$  wide shear bands. The microscopic shear band width increases by a tearing of the microvoid initiation sites. These shear bands cease to widen or thicken and become only longer when their width approaches  $\sim 100 \text{ nm}$ . This phenomenon may be related to unique stress-field conditions at the shear-band initiation regions. The dimensions of the microscopic shear bands suggest that only polymer chain segments of a few monomer units rather than any larger morphological entities are the basic units involved in the flow processes in this polymer.



**Figure 2** Diameter of microvoid shear-band initiation site as a function of shear-band length for BTAD-polyimide.

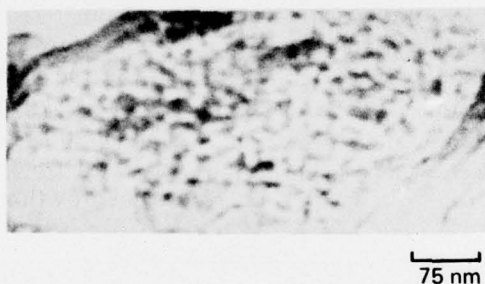
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The ability of polyimides to fibrillate increases the wear resistance of these material as aircraft wire insulation. The in-service polymer-polymer wear processes involve shearing off platelets which protrude above the general contour of the polymer surfaces. Electron microscope studies of the wear processes reveal that fibrils often hold the platlets onto the surface which enhances the wear resistance. Such fibrillation is not affected by service environment conditions.

### Epoxies

Both DGEBA-DETA and TGDDM-DDS epoxies deform and fail by a crazing process [17]. (These glasses are not highly crosslinked because of the steric and diffusional restrictions during polymerization and network formation.) Crazes were observed in films either strained directly in the electron microscope or strained on a metal substrate. The fracture topographies of these epoxies fractured as a function of temperature and strain-rate are interpreted in terms of a crazing process. A coarse fracture topography initiation region results from void growth and coalescence through the center of a simultaneously growing, poorly developed craze which consists of coarse fibrils. A surrounding, smooth, slow-crack-growth mirror region results from crack propagation either through the center or along the craze-matrix boundary interface of a thick, well-developed craze consisting of fine fibrils.

From straining films directly in the electron microscope, DGEBA-DETA epoxies were found to consist of 6-9 nm diameter particles which remain intact when flow occurs within craze fibrils. It is suggested that these particles are intramolecularly crosslinked, molecular domains which form during the initial stages of polymerization and later interconnect to form larger network morphological entities. A network of these particles within a craze fibril is illustrated in the bright-field transmission electron micrograph in Fig. 3. The TGDDM-DDS epoxies possess larger  $\sim 1 \mu\text{m}$  regions of high crosslink density.



**Figure 3 Bright-field transmission electron micrograph of strained network structure of 6-9 nm particles in DGEBA-DETA epoxy.**

The TGDDM-DDS epoxies also deform to a limited extent by shear banding. Regular right-angle steps were observed in the fracture topography initiation region, as illustrated in Fig. 4. This topography was observed in  $\sim 20\%$  of all room-temperature fractures and  $\sim 40\%$  of all fractures at  $150^\circ\text{C}$  ( $T_g \approx 250^\circ\text{C}$ ). Shear band propagation in these crosslinked glasses produces structurally weak planes because of bond cleavage caused by molecular flow. The craze or crack jumps into these structurally weak planes.

The crazing process in these epoxies is enhanced by absorbed moisture. The absorbed water lowers the craze cavitation stress and allows crazes to propagate at lower stresses. The cavities formed at the craze tip serve as a sink for water absorption, and the porous craze structure allows rapid diffusion of water to the craze tip. Such phenomena must be considered in any durability predictions of these glasses in high humidity environments.

### Conclusions

(1) The flow characteristics of polycarbonate are controlled by (1) the ease of shear band deformation which depends on free-volume and previous thermal history and (2) surface crazes whose characteristics depend on exposure to organics, thermal history, and surface crystallization and fabrication stresses.





10  $\mu$ m

**Figure 4** Scanning electron micrograph illustrating right-angle steps in the fracture topography initiation region of TGDDMS-DDS epoxies.

(2) PODPPMI and BTAD polyimides deform and fail in the bulk by crazing with extensive fibrillation. Polymer chain segments of only a few monomer units are the basic units involved in the shear-band flow processes in BTAD-polyimide.

(3) DGEBA-DETA and TGDDM-DDS epoxies predominantly deform and fail by crazing with regions of high crosslink density remaining intact during the flow processess. Right-angle steps in the fracture topography initiation region of the TGDDM-DDS epoxy suggest that shear-band deformation also occurs in this glass. Craze cavitation and growth are enhanced in these epoxies by the presence of absorbed water.

#### Acknowledgements

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